

Sonication-time dependence of sonoluminescence spectrum from Na atom in surfactant solutions

界面活性剤溶液中 Na 原子からのソノルミネセンス：超音波照射時間依存性

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1. Introduction

Sonoluminescence (SL) can be used as a spectroscopic probe of species produced at bubble collapse. Studies of SL from alkali-metal salt solutions have revealed emission from the excited alkali-metal atoms [1]. The origin of emission, however, has not been fully understood. In a surfactant solution containing Na⁺ ion, such as sodium dodecyl sulfate (SDS), the intensity of Na emission is known to be enhanced because of the high local concentration of Na⁺ ions around bubble surfaces which are adsorbed by surfactant molecules [2]. Detailed spectra are to be explored for understanding Na emission mechanism.

We observed SL spectra from SDS solutions saturated with Ar gas at the frequencies of 148 kHz as a function of sonication-time, the total of which is 30 minutes. The spectra revealed that the Na emission consists of two components, shifted broadened lines and unshifted narrow lines. The results suggest that the two components originate from different environments, although both of them are in gas phase.

2. Experimental

We measured SL spectra in the 560 - 620 nm range from SDS solutions with concentration of 10 mM. We used a sandwich-type transducer of 148 kHz. The size of the sample container was 46 mm in diameter and 150 mm in length. The top and bottom faces of the cell were equipped with a quartz glass window and the transducer, respectively. The temperature of the sample was maintained at 15 °C by circulating water. The solution was strictly degassed, and then re-gassed with Ar gas for a day. Since the sample container was closed without air, no air was introduced during the experiments. The signal from a function generator was amplified using a power amplifier. Emitted light was analyzed using a system of a monochromator and a cooled-CCD detector. The instrumental bandwidth was estimated to be 0.315 nm from the measurement of the He-Ne laser line. The spectral response was calibrated for detection efficiency against a standard halogen lamp. The total ultrasonic power was determined by calorimetry.

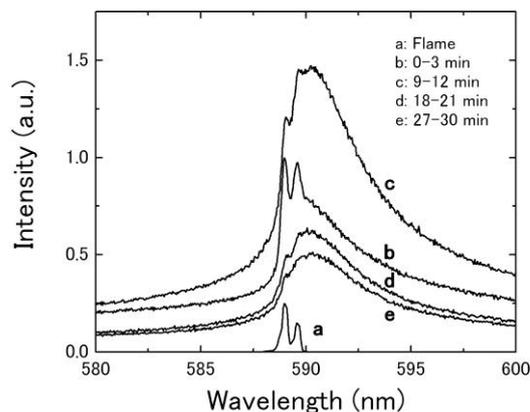


Fig. 1 Spectra of Na atom emission from SDS solutions at the sonication time interval of 9 minutes. The line “a” denotes the spectrum obtained from NaCl in a flame

3. Results and discussion

Figure 1 shows SL spectra of Na emission from SDS solutions at an ultrasonic power of 4.7 W. During 3 minutes of the start of sonication, a typical spectrum of Na doublet was observed, which is similar to that from NaCl solutions [1]. As sonication time progresses, the spectral shape considerably changed. This spectrum variation indicates that the Na emission is composed of two components, one of which is broadened lines and the other is narrow lines. The former shifted from original D lines to red side and broadened asymmetrically. The latter showed no shift, and its line width nearly equals to that of flame spectrum. As seen in Fig. 1, the narrow lines gradually disappeared with the sonication-time. Eventually, the only broadened line remained.

Figure 2 indicates the total intensity of Na emission as a function of sonication-time at ultrasonic powers of 0.4, 2.6, 4.7 and 9.1 W. The intensity of Na emission decreased with sonication-time except for the case of 4.7 W. The increase in intensity around 9 minutes at 4.7 W can be explained by electrostatic effects of ionic solutes like SDS [2]. Adsorption of SDS to bubble surface creates highly-charged bubble which repels each other. This effect prevents coalescence and clustering of bubbles, leading to an increase in the

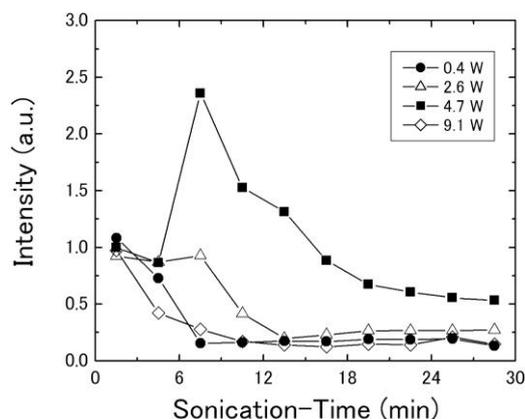


Fig. 2 Intensity of Na emission as a function of sonication-time for various ultrasonic powers.

number of bubbles undergoing violent collapse. On the other hand, the observed quenching with sonication time is likely to result from an accumulation of some gases decomposed from SDS inside bubbles. The mechanism can be understood as follows using a droplet model [1]. SDS solutes adsorbed to the bubble surface would be incorporated into the bubble as droplets including dense Na^+ ion. These droplets may be easily generated in SDS solutions due to the low surface tension of bubbles. These SDS solutes in bubbles are decomposed by heat at bubble collapse, which generates decomposition gases such as hydrogen and methane. These gases build up over many cycles of bubble oscillation. In fact, the decrease of number of SDS molecules in solutions with sonication time and the generation of these decomposition gases was reported [3]. As a result, these gases deactivate excited Na atoms in the bubble, since these gases have a quenching effect of alkali-metal emission [4].

The most interesting feature seen in Fig. 1 is that the narrow lines efficiently vanished with respect to broadened lines as sonication time advances. We numerically separated the narrow lines and the broadened lines, assuming that the line width of narrow line is the same as that of flame spectrum from NaCl and the broadened line can be expressed by overlapped gaussian function. **Figure 3** represents relative intensity of narrow line to broadened line as a function of sonication time for various ultrasonic powers. It is clearly seen that the relative intensity of narrow line decreased with sonication time. The tendency was more prominent at higher ultrasonic power. Under higher ultrasonic power, production of decomposition gases from SDS solutes may be promoted by higher temperature at bubble collapse because the bubble collapse becomes more violent. Thus, the results suggest that the narrow lines are more sensitive to gas content within bubble than broadened lines.

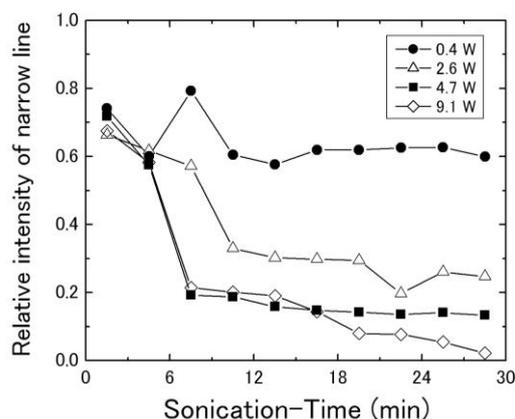


Fig. 3 Relative intensity of narrow lines to broad lines with sonication-time for various ultrasonic powers.

Recent works [1] have clarified that the origin of alkali-metal emission is likely to be in gas phase. Hayashi and Choi [5] concluded that the broadened lines come from gas phase because the broadened lines strongly depend on the kind of rare-gas perturber in the bubble. The present results suggest that the narrow lines also originate from gas phase although the emitting condition of two components will be different.

4. Conclusion

SL spectra from SDS aqueous solutions were observed for the total sonication time of 30 minutes at 148 kHz with various ultrasonic powers. The spectra showed that the Na emission consists of two components, shifted broadened lines and unshifted narrow lines. The total intensity of Na emission essentially decreased with sonication time except for temporary increase at 4.7 W. The decrease in intensity is caused by the accumulation of quenching gas within bubble, which are produced by decomposition of SDS solutes at bubble collapse. The narrow line disappeared more efficiently than broadened lines with sonication time. The results suggest that the narrow line is more sensitive to gas content within bubble than broadened lines. We conclude that not only broadened lines but narrow lines come from gas phase origin although the emitting condition of the two will be different.

References

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